

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



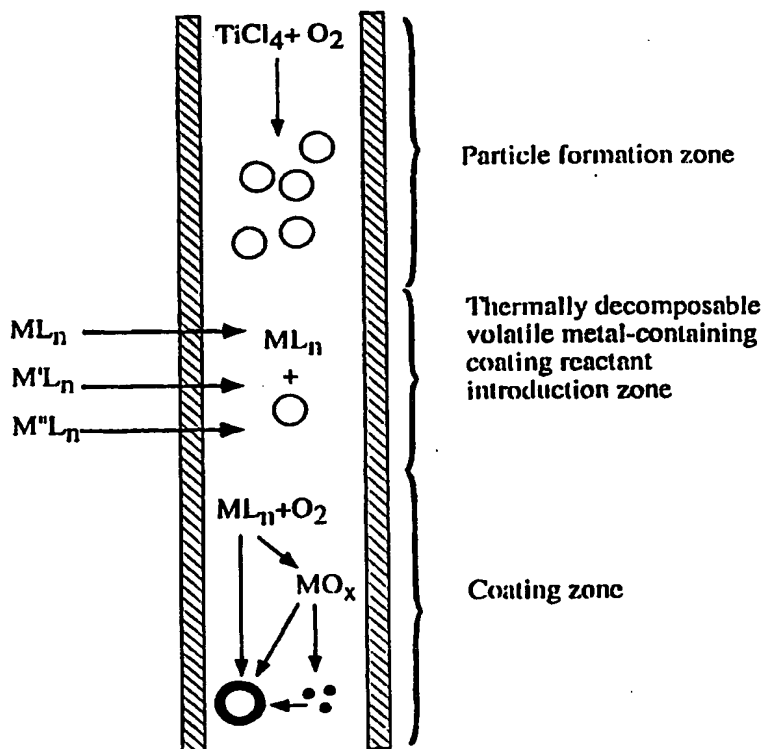
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B05D 7/00, C23C 16/00, C01G 23/00, 23/047		(11) International Publication Number: WO 96/36441
A1		(43) International Publication Date: 21 November 1996 (21.11.96)
(21) International Application Number: PCT/US96/07886		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 17 May 1996 (17.05.96)		
(30) Priority Data: 08/443,055 17 May 1995 (17.05.95) US		
(71) Applicant: KEMIRA PIGMENTS, INC. [US/US]; President Street Extension, Savannah, GA 31404 (US).		
(72) Inventors: KODAS, Toivo; 11102 San Rafael N.E., Albuquerque, NM 87122 (US). POWELL, Quint; 1144 Princeton N.E., Albuquerque, NM 87106 (US). ANDERSON, Bruce; 139 Grays Creek Drive, Savannah, GA 31410 (US).		
(74) Agents: HUCKETT, Gudrun, E. et al.; Robert W. Becker & Associates, Suite 200, 5300 Sequoia N.W., Albuquerque, NM 87120 (US).		Published With international search report. With amended claims.

(54) Title: COATING OF TiO₂ PIGMENT BY GAS-PHASE AND SURFACE REACTIONS

(57) Abstract

In a process for making pigment-grade TiO₂ coated with a metal oxide, a thermally decomposable volatile titanium-containing precursor is introduced into a reactor. The titanium-containing precursor is thermally decomposed within the reactor to form TiO₂ pigment particles. Subsequently, one or more thermally decomposable volatile metal-containing coating precursors are injected into the reactor. The one or more metal-containing coating precursors are reacted within the reactor to form a coating of the one or more metal oxides on the TiO₂ pigment particles.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CJ	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

COATING OF TiO₂ PIGMENT BY GAS-PHASE AND SURFACE
REACTIONS

Technical Field

5 This invention pertains to a process of coating titanium dioxide particles with metal oxides by gas-phase reaction.

Background Art

10 The gas-phase reaction of TiCl₄ and O₂ is used to make particulate TiO₂, often of a size useful as a white pigment. The pigment particles are usually not used in typical applications such as paint without first coating them with materials including, but not limited to, SiO₂, Al₂O₃, and mixtures thereof. To coat the particles, they are
15 typically collected from the gas and dispersed in a liquid where the coating is applied by precipitation. This liquid-phase coating process often results in coatings with high surface areas, high oil absorption, and non-uniform
20 thickness.

U.S. Patent 4,803,056 describes a method for increasing the capacity of a titanium dioxide producing process. Titanium tetrachloride is added at a second point in the system downstream of the main inlet for titanium tetrachloride to increase the yield of TiO₂. The process is
25 exclusively used for the production of uncoated titanium dioxide. The addition of other reagents at the second point of introduction in order to produce a coating on the TiO₂ particles is not
30 suggested or disclosed.

Hung and Katz (J. Mater. Res., 7, 1861 (1992)) disclose a process for forming coated

- 2. -

particles in a flame. For example, non-pigmentary TiO_2 can be coated with SiO_2 in a flame reactor whereby TiCl_4 and SiCl_4 are added simultaneously into the same flame. The reaction conditions must be carefully adjusted such that TiO_2 condenses before SiO_2 in order to achieve a coating of SiO_2 on the already formed TiO_2 particles. It is difficult to reliably produce SiO_2 -coated TiO_2 particles of a uniform quality in terms of size and coating hardness with this process.

It is therefore an object of the present invention to provide a simple and reliable process for coating TiO_2 pigment particles in the gas phase to give coatings with low surfaces areas, low oil absorption, and uniform thickness.

Disclosure of the Invention

The process for making pigment-grade TiO_2 coated with a metal oxide according to the present invention is primarily characterized by the following steps:

introducing a thermally decomposable volatile titanium-containing precursor into a reactor;

thermally decomposing the titanium-containing precursor within the reactor to form TiO_2 pigment particles;

subsequently injecting at least one thermally decomposable volatile metal-containing coating precursor into the reactor; and

reacting the at least one metal-containing coating precursor within the reactor to form a coating of at least one metal oxide on the TiO_2 pigment particles.

- 3 -

Preferably, the coating is selected from the group consisting of SiO_2 , Al_2O_3 , ZrO_2 , and mixed metal oxide. The mixed metal oxide is expediently $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$ with $x = 0-1$ and $y = 0-1$.

5 The titanium-containing precursor is selected from the group consisting of TiCl_4 , TiBr_4 , and $\text{Ti}(\text{OR})_4$, wherein R is an alkyl group.

10 The method advantageously further comprises the step of adding a thermally decomposable volatile aluminum-containing precursor to the titanium-containing precursor to form Al-doped TiO_2 . As is well known in the art, water may also be added to control the particle size of the formed TiO_2 pigment particles.

15 The metal-containing coating precursor is selected from the group consisting of SiX_4 , AlX_3 , and ZrX_4 , wherein X is Cl, Br or OR, R being an alkyl group. However, other metal-containing coating precursors can be used equally
20 successfully. For example, they may be selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal β -diketonates,
25 all well known to a person skilled in the art. It is also possible to use metal carbonyls, metal oxyhalides, and metal hydrides.

30 The method further comprises the step of adding a co-reactant, preferably water, to the metal-containing coating precursor. It is known to a person skilled in the art that water may be used to modify or control the reaction of the coating precursor.

- 4 -

The reactor is advantageously a tubular flow reactor.

5 The method further comprises the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a TiO_2 -formation zone of the tubular flow reactor.

10 The injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of a coaxial tube of the tubular flow reactor, and a radially extending injection port.

15 In a preferred embodiment of the present invention, at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

20 The inventive method according to another embodiment further comprises the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing coating precursors downstream of a TiO_2 -formation zone of the tubular flow reactor.

25 The coating precursors may be injected as mixtures, or separately but simultaneously at the same point in the reactor, or may be injected separately at different points in the reactor to produce mixed oxide coatings or to produce a

30 coating comprising separate layers of metal oxides. The injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the

- 5 -

tubular flow reactor, and a radially extending injection port.

Preferably, each separate coating layer has a thickness of 1-100 nm. Advantageously, the coating has a total thickness of 1-100 nm.

The step of thermally decomposing includes the step of heating by fuel combustion, by conduction or by a plasma arc for initiating the formation of TiO_2 .

The step of introducing the titanium-coating precursor includes the step of selecting a first and a second location of introduction, wherein the second location is arranged downstream of the first location.

The step of introducing the titanium-containing precursor and/or the step of injecting the metal-containing coating precursor may include the step of employing a carrier gas, for example, oxygen.

Preferably, the method further comprises the step of collecting the TiO_2 pigment particles downstream of the flow reactor.

Advantageously, the reactor is maintained at atmospheric pressure during the inventive process. It is also possible to maintain less than atmospheric pressure (vacuum) within the reactor or perform the inventive process at a pressure of 1 to 10 atm (atmospheres) within the reactor.

The present invention describes a gas-phase method for making coated pigment grade TiO_2 . It allows multi-component coatings and multilayer coatings. The coatings produced by the inventive

- 6 -

process are dense and have low oil absorption. The inventive process eliminates the need to collect the particles before the coating can be applied thereby simplifying the manufacturing process.

5 According to the present invention TiO_2 pigment particles are produced by a gas-phase reaction of titanium-containing precursors, for example, TiX_4 , suspended in a gas stream and are
10 then coated with a coating of metal oxide(s) produced by gas-phase and surface reactions of thermally decomposable volatile metal atom- or ion-containing coating reactants introduced at a
15 single point or multiple points into a tubular flow system at a location downstream of the formation zone in which the TiO_2 pigment particles are fully formed.

The inventive system or apparatus consists of three sections including sequentially:
20 a tubular flow formation zone in which the TiO_2 particles are formed, a zone in which the thermally decomposable volatile metal atom- or ion-containing coating reactants (precursors) are introduced into the gas stream carrying the TiO_2
25 particles to be coated, and a coating zone in which the TiO_2 particles are coated by the metal oxide(s) being formed from the metal-containing coating precursor(s).

30 In a first step, the titanium dioxide particles are formed by gas-phase reaction. Subsequently, the volatile metal-containing coating precursors are injected which react in the gas phase as well as on the surface of the

- 7 -

titanium dioxide particles to form a coating. The coated particles are then collected at the exit of the flow reactor. Thus, the invention described here relies on sequential particle formation and particle coating.

Brief Description of the Drawing

The object and advantages of the present invention will appear more clearly from the following specification in conjunction with the accompanying drawing, in which the only Figure schematically shows the system for coating particles according to the present invention for a specific embodiment.

Best Modes for Carrying out the Invention

The present invention will now be described in detail with the aid of several specific embodiments utilizing the only Figure in which a specific embodiment is illustrated.

The inventive system consists of the following components: a pigment particle generator (particle formation zone), an introduction zone for the thermally decomposable volatile metal-containing coating precursor (reactant), and a coating zone. In the particle formation zone, TiCl_4 reacts with O_2 to form respective TiO_2 particles (illustrated as small circles). The drawing shows the introduction of three thermally decomposable volatile metal-containing coating reactants downstream of the particle formation zone: ML_n , $\text{M}'\text{L}_n$, and $\text{M}''\text{L}_n$ where M, M', M'' represent a metal atom and L represents a ligand attached to the metal atom. However, the reaction of only one coating reactant ML_n is shown. It is

- 8 -

schematically shown that the reaction to form the metal oxide can take place in the gas phase (formation of small particles, illustrated by small cross-hatched circles) which are then captured by the preformed TiO_2 particles to form the coating or can take place at the surface of the TiO_2 particles resulting in a direct coating of the TiO_2 particle (the produced coating is schematically represented by cross-hatching).

Preferred compounds are, for example, SiCl_4 , SiBr_4 , Si(OR)_4 , AlCl_3 , AlBr_3 , Al(OR)_3 , ZrCl_4 , ZrBr_4 , and Zr(OR)_4 . It is obvious to those skilled in the art that other types of precursors of various structures can be used, for example, coating precursors with organic ligands such as metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal β -diketonates or coating precursors with inorganic ligands such as metal carbonyls, metal oxyhalides, and metal hydrides. The given compounds are examples only and not meant to limit the scope of the inventive process

The drawing shows the sequential nature of the process in which the particles are formed first, followed by introduction of the thermally decomposable volatile metal-containing coating reactants, and then coating. It is also obvious that only one or a plurality of thermally decomposable volatile metal-containing coating reactants can be used, as desired and needed for the TiO_2 pigment product properties. Thus, the invention is not limited with respect to the

- 9 -

number of thermally decomposable volatile metal-containing coating reactants that can be used, the order in which they are introduced into the reactor, or the type of thermally decomposable volatile metal-containing coating reactant.

It is also possible to use an additional metal compound as a dopant together with the titanium-containing precursor. For example, TiCl_4 as a titanium precursor can be mixed with AlCl_3 , introduced into the reactor with oxygen (carrier gas) at a temperature of about 900°C or higher, and reacted in a tubular flow system to give TiO_2 particles containing Al. It is obvious to those skilled in the art that other types of dopants can be added to the titanium-containing precursor without departing from the scope of the present invention. In this context it should also be mentioned that water can be added, as is well known in the art, in order to help adjust or control the TiO_2 particle size.

It is well known to persons skilled in the art that the particle formation and particle coating within the reactor occur over a short period of time. The gas stream exiting from the reactor is cooled to allow collection of the coated particles.

The gist of the present invention is the addition (injection) of a thermally decomposable volatile metal-containing coating reactant into a reactor tube at a location downstream of the zone in which the TiO_2 particles are formed, but where the temperature is still high enough to cause reaction of the thermally decomposable volatile

- 10 -

metal-containing coating reactants both in the gas phase and on the surfaces of the TiO_2 pigment particles.

5 It is possible to add only a single thermally decomposable volatile metal-containing coating reactant, such as SiCl_4 , in order to give a coating of one material (SiO_2 in the given example).

10 However, it is also possible to add two thermally decomposable volatile metal-containing coating reactants at the same time to give a single coating which is a mixed oxide of the two metals. For example, SiX_4 and AlX_3 can be added together resulting in a mixed oxide $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$,
15 wherein essentially any ratio between the two oxides is possible. In this case it is desirable to match the reaction temperatures of the thermally decomposable volatile metal-containing coating reactants to allow reaction at the same
20 location in the reactor.

In another embodiment of the present invention, two or more thermally decomposable volatile metal-containing coating reactants are added sequentially to give a coating comprised of
25 two or more layers of individual metal oxides.

The invention can be carried out in a variety of apparatus configurations. The preferred embodiment is a tubular flow system in which the thermally decomposable volatile metal-containing coating reactants are introduced from
30 the exterior of the reactor tube into the reactor tube at points downstream of the zone in which the TiO_2 particles are formed but where the

- 11 -

temperature is still high enough to cause reaction of the thermally decomposable volatile metal-containing coating reactants both in the gas phase and on the surfaces of the particles.

5 Various approaches can be used to introduce the thermally decomposable volatile metal-containing coating reactants into the reactor. For example, the thermally decomposable volatile metal-containing coating reactants can be
10 added through a porous wall or through radially extending injection points. It is also possible to use coaxial injection. Those skilled in the art realize other methods that are also equally viable.

15 The temperature at which the thermally decomposable volatile metal-containing coating reactants are to be decomposed must be sufficiently high in order for the coating reactants to react at the surface of the TiO_2
20 particles or for the particles of the coating material, formed in the gas phase, to be able to collide with the TiO_2 pigment particles and fuse into their surfaces. Temperatures that are too low result in formation of separate particles
25 comprised of the coating material that are not incorporated into the coating. Temperatures that are too high result in reaction of the coating material with the particle to be coated, i.e., the metal(s) of the coating material and the TiO_2
30 particle react to form mixed metal oxide phases thus degrading the TiO_2 pigment particle properties.

For the coating of TiO_2 with SiO_2 using

- 12 -

SiCl₄, the temperature must be greater than 1300°C. When TiO₂ is to be coated with Al₂O₃, the temperature must be greater than 1100°C. For coating TiO₂ with a mixed Si/Al oxide, the temperature must be greater than 1200°C. However, in any case, the temperature must not be too high in order to prevent interdiffusion and/or reaction between TiO₂ and the coating material.

The flow reactor can be heated to the required reaction temperature by conventional methods such as fuel combustion, conduction, a plasma arc or other means well known to a person skilled in the art.

Especially for large scale production processes, it is known in the art to use the energy derived from the exothermic reaction of the Ti-containing precursor with oxygen for heating the flow reactor to the desired reaction temperature when the gaseous reactants (Ti-containing precursor and oxygen) are preheated to a suitable preheating temperature. Of course, the exothermicity of the reaction aids in reaching the required temperature in all possible process variations.

The inventive process can be carried out under various pressures. The reactor can simply be maintained at atmospheric pressure during the inventive process. It is also possible to maintain less than atmospheric pressure (vacuum) within the reactor or perform the inventive process at a pressure of 1 to 10 atm (atmospheres) within the reactor.

Example 1. Formation of TiO₂ particles coated with

- 13 -

SiO₂.

A tubular flow reactor was used at a temperature of 1500 °C. Oxygen gas (carrier gas) was guided through TiCl₄ to vaporize and introduce TiCl₄ into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 seconds. The gas mixture reacted to form TiO₂ particles in the reactor.

Liquid SiCl₄ was vaporized by heating at 25°C and introduced as a vapor into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed the SiCl₄ to be introduced into the reactor in a region where the temperature was near 1500 °C. The SiCl₄ reacted both in the gas phase and on the surfaces of the formed TiO₂ particles. The gas phase reaction of the metal-containing coating precursor resulted in the formation of small metal oxide particles which were captured by the TiO₂ particles and incorporated into the surface as a coating by sintering. Because of the small size of the metal oxide particles, sintering was rapid. The coated TiO₂ pigment particles were collected on a filter after exiting the reactor.

The surface reaction resulted in the direct deposition of a uniform continuous coating with a thickness of 10 nm as shown by Transmission Electron Microscopy. The composition of the coating was confirmed by energy dispersive spectroscopy which showed only Si and O. X-ray diffraction showed only TiO₂ and confirmed that the coating process did not degrade the properties

- 14 -

of the pigment by forming additional undesired phases.

Example 2. Formation of TiO_2 particles coated with Al_2O_3 .

5 A tubular flow reactor was used at a temperature of 1500 °C. Oxygen (carrier gas) was guided through TiCl_4 to vaporize and introduce TiCl_4 into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 sec. The gas mixture reacted to form TiO_2 particles in the reactor.

15 AlCl_3 was vaporized by heating at less than 250 °C and passing a carrier gas over the powder. The vapor was introduced into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed AlCl_3 to be introduced into the reactor in a region where the temperature was near 1500°C. AlCl_3 reacted both in the gas phase and on the surfaces of the formed TiO_2 particles. The gas phase reaction of the metal-containing coating precursor AlCl_3 resulted in the formation of small particles of Al_2O_3 which were captured by the TiO_2 particles and incorporated into the surface as a coating by sintering. Because of the small size of the Al_2O_3 particles, sintering was rapid. The particles were collected on a filter after exiting the reactor.

30 The surface reaction resulted in the direct deposition of a uniform continuous coating with a thickness of 10 nm as shown by Transmission Electron Microscopy. The composition of the

- 15 -

coating was confirmed by energy dispersive spectroscopy which showed only Al and O. X-ray diffraction showed only TiO_2 , and confirmed that the coating process did not degrade the properties of the TiO_2 pigment particles by forming additional undesired phases.

Example 3. Formation of TiO_2 particles coated with $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$.

A tubular flow reactor was used at a temperature of 1500 °C. Oxygen (carrier gas) was guided through TiCl_4 to vaporize and introduce TiCl_4 into the carrier gas. The resulting gas mixture was then introduced into a reactor tube with a residence time of less than 10 sec. The gas mixture reacted to form TiO_2 particles in the reactor.

SiCl_4 was vaporized by heating at 25°C without a carrier gas, and AlCl_3 was vaporized by heating at less than 250°C with carrier gas flowing over the AlCl_3 powder. The streams were combined and introduced as a vapor into the hot region of the reactor using tubes inserted from the exit of the reactor. This allowed the SiCl_4 and AlCl_3 to be introduced into the reactor in a region where the temperature was near 1500°C. SiCl_4 and AlCl_3 reacted both in the gas phase and on the surfaces of the particles. The gas phase reaction resulted in the formation of small metal oxide particles which were captured by the formed TiO_2 particles and incorporated into the surface as a coating by sintering. Sintering was rapid because of the small size of the metal oxide particles. The coated TiO_2 pigment particles were

- 16 -

collected onto a filter after exiting the reactor.

5 The surface reaction resulted in the
direct deposition of a uniform continuous coating
with a thickness of 10 nm as shown by Transmission
Electron Microscopy. The composition of the
coating was confirmed by energy dispersive
spectroscopy which showed only Si, Al and O. X-
ray diffraction showed only TiO_2 and confirmed
that the coating process did not degrade the
10 properties of the pigment by forming additional
undesired phases.

15 The present invention is, of course, in
no way restricted to the specific disclosure of
the specification, examples and drawings, but also
encompasses any modifications within the scope of
the appended claims.

- 17 -

CLAIMS:

1. A process for making pigment-grade TiO_2 coated with a metal oxide, said method comprising the steps of:

5 introducing a thermally decomposable volatile titanium-containing precursor into a reactor;

thermally decomposing the titanium-containing precursor within the reactor to form TiO_2 pigment particles;

10 subsequently injecting at least one thermally decomposable volatile metal-containing coating precursor into the reactor; and

15 reacting the at least one metal-containing coating precursor within the reactor to form a coating of at least one metal oxide on the TiO_2 pigment particles.

2. A method according to claim 1, wherein said coating is selected from the group consisting of SiO_2 , Al_2O_3 , ZrO_2 , and mixed metal oxide.

3. A method according to claim 2, wherein the mixed metal oxide is $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$.

4. A method according to claim 1, wherein the titanium-containing precursor is selected from the group consisting of TiCl_4 , TiBr_4 , and $\text{Ti}(\text{OR})_4$ wherein R is an alkyl group.

5. A method according to claim 1, further comprising the step of adding a thermally decomposable volatile aluminum-containing compound to the titanium-containing precursor to form Al-doped TiO_2 .

6. A method according to claim 1,

- 18 -

wherein the metal-containing coating precursor is selected from the group consisting of SiX_4 , AlX_3 , and ZrX_4 , wherein X is Cl, Br or OR.

7. A method according to claim 6, further comprising the step of adding a co-reactant to the metal-containing coating precursor.

8. A method according to claim 7, wherein the co-reactant is water.

9. A method according to claim 1, wherein the reactor is a tubular flow reactor.

10. A method according to claim 9, further comprising the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a TiO_2 -formation zone of the tubular flow reactor.

11. A method according to claim 10, wherein the injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

12. A method according to claim 10, wherein at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

13. A method according to claim 1, further comprising the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing

- 19 -

5 coating precursors downstream of a TiO_2 -formation zone of the tubular flow reactor to produce a coating comprising separate layers of metal oxides.

14. A method according to claim 13, wherein the injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the
5 tubular flow reactor, and a radially extending injection port.

15. A method according to claim 13, wherein each separate layer of the coating has a thickness of 1-100 nm.

16. A method according to claim 1, wherein the coating has a total thickness of 1-100 nm.

17. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating by fuel combustion for initiating the formation of TiO_2 .

18. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating by conduction for initiating the formation of TiO_2 .

19. A method according to claim 1, wherein the step of thermally decomposing includes the step of heating with a plasma arc for initiating the formation of TiO_2 .

20. A method according to claim 1, wherein in the step of introducing the titanium-containing precursor includes the step of selecting a first and a second location of
5 introduction, wherein the second location is

- 20 -

arranged downstream of the first location.

21. A method according to claim 1, wherein the step of introducing includes the step of employing a carrier gas.

22. A method according to claim 1, wherein the step of injecting includes the step of employing a carrier gas.

23. A method according to claim 1, further comprising the step of collecting the TiO₂ pigment particles downstream of the flow reactor.

24. A method according to claim 1, further comprising the step of maintaining atmospheric pressure within the reactor.

25. A method according to claim 1, further comprising the step of maintaining less than atmospheric pressure within the reactor.

26. A method according to claim 1, further comprising the step of maintaining a pressure of 1 to 10 atm within the reactor.

27. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal β -diketonates.

28. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal carbonyls, metal oxyhalides, and metal hydrides.

AMENDED CLAIMS

[received by the International Bureau on 07 October 1996 (07.10.96);
original claims 1, 2, 6 and 17-19 amended; remaining claims unchanged (4 pages)]

1. A process for making pigment-grade TiO_2 coated with
a metal oxide, said method comprising the steps of:

introducing a thermally decomposable volatile
titanium-containing precursor into a reactor;

5 thermally decomposing in the presence of oxygen the
titanium-containing precursor within the reactor to form TiO_2
pigment particles;

subsequently injecting at least one thermally
decomposable volatile metal-containing coating precursor into the
10 reactor; and

thermally decomposing in the presence of oxygen the
at least one metal-containing coating precursor within the reactor
to form a coating of at least one metal oxide on the TiO_2 pigment
particles.

2. A method according to claim 1, wherein said coating
is selected from the group consisting of SiO_2 , Al_2O_3 , ZrO_2 , and
mixed metal oxide of at least two of the metals Si, Al, and Zr.

3. A method according to claim 2, wherein the mixed
metal oxide is $[\text{SiO}_2]_x[\text{Al}_2\text{O}_3]_y$.

4. A method according to claim 1, wherein the titanium-
containing precursor is selected from the group consisting of TiCl_4 ,
 TiBr_4 , and Ti(OR)_4 wherein R is an alkyl group.

5. A method according to claim 1, further comprising
the step of adding a thermally decomposable volatile aluminum-
containing compound to the titanium-containing precursor to form
Al-doped TiO_2 .

6. A method according to claim 1, wherein the metal-
containing coating precursor is selected from the group consisting
of SiX_4 , AlX_3 , and ZrX_4 , wherein X is Cl, Br or OR, wherein R is an
alkyl group.

7. A method according to claim 6, further comprising the step of adding a co-reactant to the metal-containing coating precursor.

8. A method according to claim 7, wherein the co-reactant is water.

9. A method according to claim 1, wherein the reactor is a tubular flow reactor.

10. A method according to claim 9, further comprising the step of selecting a location for an injection element for injecting the at least one metal-containing coating precursor downstream of a TiO_2 -formation zone of the tubular flow reactor.

11. A method according to claim 10, wherein the injection element is selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

12. A method according to claim 10, wherein at least two of the metal-containing coating precursors are injected at a single point through an injection element selected from the group consisting of a slot and a porous wall segment.

13. A method according to claim 1, further comprising the step of selecting a plurality of locations for injection elements for injecting at least two of the metal-containing coating precursors downstream of a TiO_2 -formation zone of the tubular flow reactor to produce a coating comprising separate layers of metal oxides.

14. A method according to claim 13, wherein the injection elements are selected from the group consisting of a slot, a porous wall element, an annular segment of coaxial tube of the tubular flow reactor, and a radially extending injection port.

15. A method according to claim 13, wherein each separate layer of the coating has a thickness of 1-100 nm.

16. A method according to claim 1, wherein the coating

has a total thickness of 1-100 nm.

17. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating by fuel combustion for initiating the formation of TiO_2 .

18. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating by conduction for initiating the formation of TiO_2 .

19. A method according to claim 1, wherein the step of thermally decomposing the titanium-containing precursor includes the step of heating with a plasma arc for initiating the formation of TiO_2 .

20. A method according to claim 1, wherein in the step of introducing the titanium-containing precursor includes the step of selecting a first and a second location of introduction, wherein the second location is arranged downstream of the first location.

21. A method according to claim 1, wherein the step of introducing includes the step of employing a carrier gas.

22. A method according to claim 1, wherein the step of injecting includes the step of employing a carrier gas.

23. A method according to claim 1, further comprising the step of collecting the TiO_2 pigment particles downstream of the flow reactor.

24. A method according to claim 1, further comprising the step of maintaining atmospheric pressure within the reactor.

25. A method according to claim 1, further comprising the step of maintaining less than atmospheric pressure within the reactor.

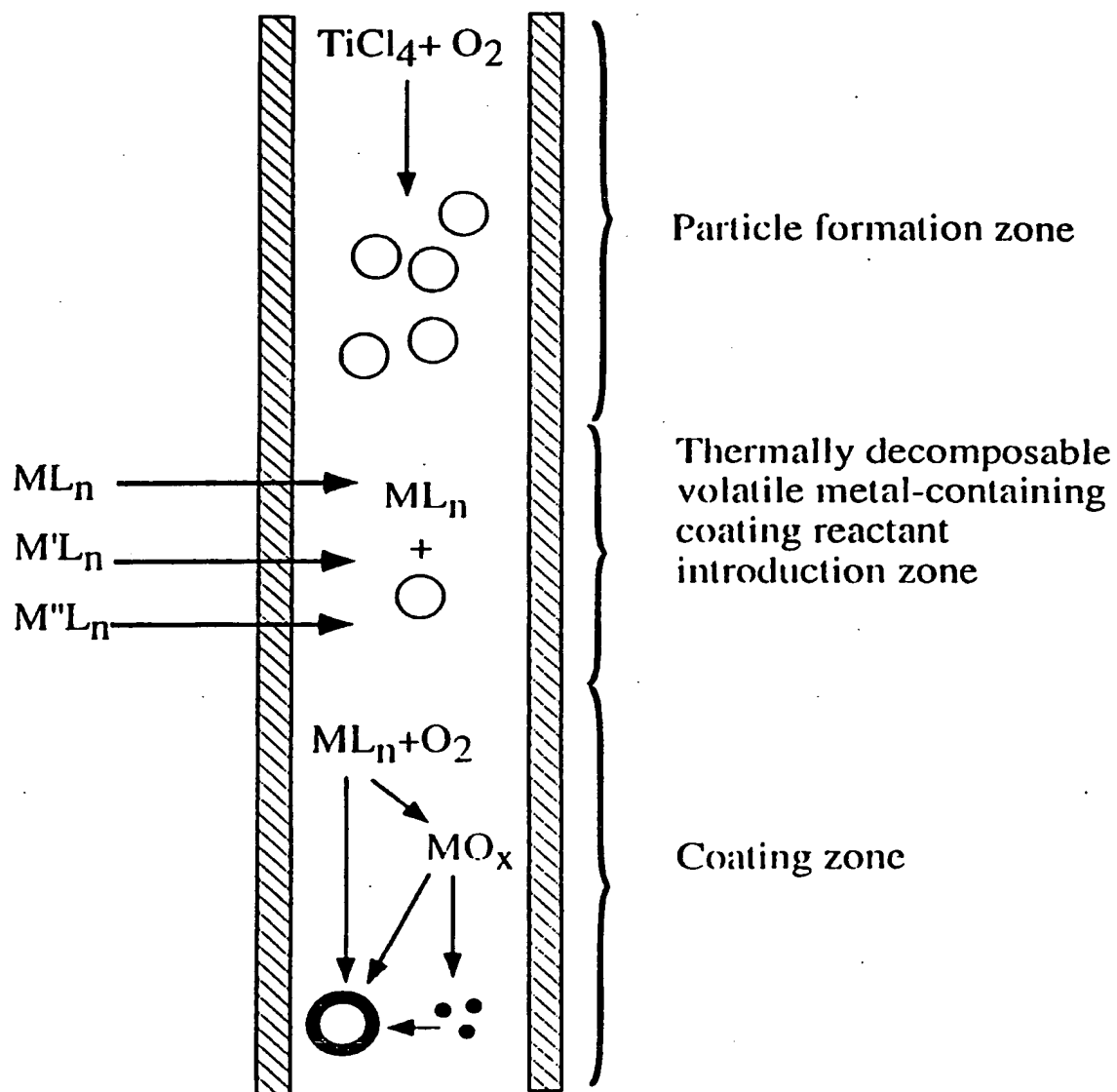
26. A method according to claim 1, further comprising the step of maintaining a pressure of 1 to 10 atm within the reactor.

5

27. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal alkyls, metal alkenyls, metal alkynes, metal allyls, metallocenes, metal cyclopentadienes, metal arenes, metal alkoxides, and metal β -diketonates.

28. A method according to claim 1, wherein the metal-containing coating precursor is selected from the group consisting of metal carbonyls, metal oxyhalides, and metal hydrides.

1 / 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/07886

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B05D 7/00; C23C 16/00; C01G 23/00, 23/047

US CL : 427/212, 215, 248.1; 423/598, 610, 611, 612, 613, 614

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/212, 215, 248.1; 423/598, 610, 611, 612, 613, 614

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS. Search terms: pigment, titanium, oxide, dioxide, metal, coating, vapor, deposition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,512,219 (STERN ET AL.) 19 May 1970, col 2, line 45 to col 4, line 56.	1-28
Y	US, A, 4,050,951 (PICCOLO ET AL.) 27 September 1977, col 2, lines 39-56; col 3, lines 12-17.	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

<p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>		<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>*G* document member of the same patent family</p>
--	--	---

Date of the actual completion of the international search

22 JULY 1996

Date of mailing of the international search report

14 AUG 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

SHRIVE BECK

Facsimile No. (703) 305-3230

Telephone No. (703) 308-0661